Investigation on U(VI) Sorption / Desorption on Nanopores Goethite, and Structures of Ferrihydrite Nano-mineral

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Most reactive surfaces in clay-dominated sediments are present within nanopores (pores of nm dimension). The behavior of geological fluids and minerals in nanopores is significantly different from those in normal non-nanoporous environments. The effect of nanopore surfaces on U(VI) sorption/desorption and reduction is likely to be significant in clay-rich subsurface environments. Our research objective is to test the hypothesis that U(VI) sorption on nanopore surfaces can be greatly enhanced by nanopore confinement environments.

We investigated sorption and desorption of uranium on both natural nanoporous and non-porous goethite. U(VI) Desorption experiments of nanoporous goethite and non-porous goethite model systems show that all the sorbed U(VI) on non-porous goethite can be easily desorbed with low bicarbonate concentration. However, the most sorbed U(VI) on nanoporous goethite can not be desorbed even with high bicarbonate concentration. 50 mM bicarbonate solutions can only desorb ~ 10% of the sorbed uranium. The results also support that sorbed U(VI) in natural FRC sediments are bonded to both nanopore surfaces (strong sorption) and non-nanopore surfaces (weak sorption). Majority of sorbed U(VI) are associated with goethite nano-crystals. If we use Dithinote-Citrate-Bicarbonate (DCB) to remove goethite nano-crystals, it also removes more than 80% of U(VI). The amounts of labile Fe by BCD method is approximately 300 umol/kg.

Ferrihydrite nano-minerals are precursors for nanoporous goethite. Mechanism for highly reactive surfaces of ferrihydrite is not well explained, because ferrihydrite structure is still not well understood. We have determined structure and defects in a natural ferrihydrite using Z-contrast imaging. With spherical aberration-corrected scanning transmission electron microscopy (STEM), we can obtain locations of Fe atoms and vacancies in ferrihydrite directly from Z-contrast images with better than 0.1 nm spatial resolution. Two polymorphs are confirmed: ferrihydrite-4H (~ 2/3) and ferrihydrite-2H (~1/3). Intergrowth of the two polymorphs can also occur with (001) as interface. The 2H polymorph has ABAB packing for oxygen atoms, and the 4H polymorph has ABAC packing with doubled unite cell parameters along *a*- and *b*-directions with respect to the 2H polymorph. All Fe atoms occupy octahedral sites. Unit cell doubling along the *a*-, *b*-, and *c*-directions in ferrihydrite-4H is resulted from the ordering between Fe and vacancy in octahedral sites. Due to structural disordering between Fe and vacancies, ferrihydrite can be considered as 2-D crystals with two strong *(hk0)* diffraction peaks. The calculated XRD pattern based on the new structural models fits observed and reported XRD patterns well. Stoichiometry of 6-line ferrihydrite is close to $Fe(III)_{0.75}(O, OH)_2$ based on occupancy fitting, i.e., between $Fe(OH)_3$ and FeOOH, instead of between FeOOH and Fe_2O_3. Z-contrast images of ferrihydrite sorbed with U(VI) show that some of the adsorbed U atoms are right on Fe-sites. It is proposed that structural disordering could be a reason for very reactive surfaces of ferrihydrite.